Thermodynamic Study of Ag,Se and Te in Copper-Matte System by Multiple Knudsen CellMass Spectrometry(多重クヌーセンセル質量分析法による銅-マット系中のAg,Se,Teの熱力学的研究)

氏名	アリレザ ザケリ Alireza Zakeri
授与学位	博士（工学）
学位授与年月日	平成１１年９月８日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）金属工学専攻
学位論文題目	Thermodynamic Study of Ag, Se and Te in Copper-Matte System by Multiple Knudsen Cell Mass Spectrometry （多重クヌーセンセル質量分析法による銅ーマット系中のAg, Se, Teの熱力学的研究）
指導教官	東北大学教授　板垣 乙未生
論文審査委員	主査　東北大学教授　板垣 乙未生　東北大学教授　井口 泰孝 東北大学教授　日野 光兀　東北大学助教授　日野 光久

論文内容要旨

1. Introduction

Thermodynamic properties of minor elements in the copper smelting systems are necessary to analyze their behavior in the volatilization and slagging phenomena. The present study has primarily aimed at the experimental determination of the limiting activity coefficients of silver, selenium and tellurium in copper mattes. For this purpose, activities of these elements have been determined at the dilute concentration range of the elements in the copper-saturated mattes of the Cu-Fe-S-X systems with varying Fe/Cu ratios. The experiments were carried out at 1473 K employing the multiple Knudsen cell mass spectrometric method. The liquidus surface of the miscibility gap and phase relations between coexisting matte and copper phases for the systems mentioned above have also been experimentally determined.

2. Multiple Knudsen Cell Mass Spectrometry

In Chapter 2, the applicability of the multiple Knudsen method to the systems of the present investigation has been discussed. This is mainly attributed to the following two merits: *(1)* the capability of the mass spectrometer in the characterization of vapors having a very low partial pressure and/or a complex nature, and *(2)* the capability of the multiple Knudsen cell assembly to deal with multi-component systems with big differences in component volatilities.

The experimental procedure for activity determination involves successive measurements of the ion intensities of the minor element at 1473 K from two samples: a sample under investigation and a reference sample. An individual activity at a given concentration of the minor element is directly calculated from the corresponding measured intensity ratio and the activity of minor element in the reference sample.

3. Critical Assessment of Activities in the Reference Systems

In Chapter 3, a critical assessment has been made to determine the activities of silver, selenium and tellurium in the corresponding copper binary alloys, which were required to serve as reference values for the main activity determinations. Activities of silver in the copper-silver binary alloys have been measured over the whole range of the alloy composition employing the multiple Knudsen cell at temperatures of 1373, 1423 and 1473 K. From the measurement of the ratio of ion intensity of copper to that of silver in a single Knudsen cell, activities of silver and copper have been also determined employing the Belton-Fruehan method, which uses the Gibbs-Duhem equation and graphical integration. A comparison between the results for the two methods showed that the activities obtained by the conventional Belton-Fruehan method might be imprecise in the systems with a significant difference in component volatilities, as in the Cu-Ag alloys. The limiting Raoultian activity coefficient of silver in liquid copper has been correlated with the absolute temperature by the expression, $\ln \gamma^{\circ}_{Ag(Cu)} = 4050/T - 1.56$, in the temperature range of 1373-1473 K.

Updated activity values of Se and Te in the copper-saturated Cu_2Se and copper-saturated Cu_2Te liquids at 1473 have been obtained as $(3.8\pm0.7)\times10^{-4}$ and $(3.0\pm0.3)\times10^{-3}$, respectively, employing the raw experimental data of a previous activity determination study by a transportation method. In the calculation, the coexistence of all Se and Te oligomers and/or polymers have been taken into account using the latest dissociation energy data corresponding to Se and Te gas molecules. In addition, the limiting activity coefficient of Se in liquid copper has been experimentally determined for the first time, to be 1.4×10^{-2} at 1473 K. For Te, an updated limiting Raoultian activity coefficient value was obtained as 1.2×10^{-1}, from the raw experimental data as described above. From the deflection at the miscibility gap boundary in the activity curves of selenium and tellurium, the solubility of Se and Te in liquid copper at 1473 K was found to be 3.6 and 8.3 at%, respectively.

4. Phase Relations between Matte and Alloy

In Chapter 4, the liquidus surface and phase relations in the miscibility gaps of the systems Cu-Fe-S, Cu-Fe-S-Ag, Cu-Fe-S-Se and Cu-Fe-S-Te, have been established at 1473 K to supplement the activity measurement data. A quenching method was adopted for this purpose and the equilibrium compositions of the conjugated phases were determined. For the Cu-Fe-S system, it has been found that the miscibility gap is much narrower in the copper side than in the matte side, with $L_{Fe}^{m/c}$=2.22 at the boundary between two- and three-phase regions. This finding rejects some of the reference data. Silver mainly distributes in the copper phase rather than in the coexisting matte phase. The distribution ratios of Ag have shown to be constant at dilute concentrations and are lowered by increasing the iron content. Se and Te have a strong preference to the matte phase. At a given iron content, the distribution of Se has shown a non-linear trend while that of Te has exhibited linearity. The addition of iron increases $L_{Se}^{m/c}$, while decreases $L_{Te}^{m/c}$.

5. Activities of Ag, Se and Te in the Cu-S-*X* Ternary System

In Chapter 5, activities of minor elements Ag, Se and Te have been experimentally determined in the Cu-Cu_2S immiscible liquids. Selenium and tellurium show extremely negative deviation from ideality while silver exhibits a positive deviation. The limiting Raoultian activity coefficients of silver in the conjugated copper and copper sulfide phases have been correlated to the absolute temperature by the expressions, $\ln [\gamma^{\circ}_{Ag}]_{Cu\text{-}S} = 3030/T - 0.87$ and $\ln \{\gamma^{\circ}_{Ag}\}_{Cu\text{-}S} = 2830/T + 0.37$, respectively, in the temperature range of 1373-1473 K. The limiting activity coefficients of Se and Te in the copper phase saturated with copper sulfide are obtained to be 6.4×10^{-3} and 7.3×10^{-2} at 1473 K, respectively. The corresponding values for the copper-saturated copper sulfide phase are 5.6×10^{-4} and 9.3×10^{-3}, respectively. The first-order interaction parameters of sulfur on Ag, Se and Te have been estimated to be 0, - 35 and - 23, respectively. Activities of $AgS_{0.5}$ in the copper sulfide phase have been calculated from the measured silver activities. A value of 0.81 is obtained for $\gamma^{\circ}_{AgS_{0.5}}$ at 1473 K when the sulfide phase is assumed to be a $CuS_{0.5-x}$ -$AgS_{0.5}$ pseudo-binary solution.

6. Activities of Ag, Se and Te in the Cu-Fe-S-*X* Quaternary System

In Chapter 6, sulfur pressures and copper activities have been measured in the miscibility gap of the parent Cu-Fe-S system. The results have been correlated with mass% of iron in the matte by the expressions

$$\log(p_{S_2}/\text{atm}) = -6.00 - 1.7\times10^{-2}(\%\text{Fe}) - 2.6\times10^{-4}(\%\text{Fe})^2, \text{ and}$$

$$a_{Cu} = 0.98 - 1.5\times10^{-4}(\%\text{Fe})^2.$$

In addition, the activities of Ag, Se and Te in iron-bearing mattes saturated with copper have been determined at 1473 K. At a given concentration, activities of Ag and Te in the copper-saturated matte increase by the addition of iron while that of Se remains unchanged. In the matte-saturated copper phase, and at a given concentration, activities of Ag, Se and Te do not change appreciably with small amounts of iron, but they are enhanced beyond about 10 at%Fe. The limiting activity coefficients in the copper-saturated matte are correlated with iron content of the matte by the following expressions.

$$\{\gamma^{\circ}_{Ag}\}_{Cu\text{-}Fe\text{-}S} = 2.29 + 2.65\times10^{-7}(\%\text{Fe})^5$$

$$\{\gamma^{\circ}_{Se}\}_{Cu\text{-}Fe\text{-}S} = -7.5$$

$$\{\gamma^{\circ}_{Te}\}_{Cu\text{-}Fe\text{-}S} = -4.72 + 7.7\times10^{-5}(\%\text{Fe})^3$$

The variation of the limiting activity coefficients of the minor elements in the copper phase has been examined, and the first-order interaction parameters of iron on silver, selenium and tellurium in liquid copper at 1473 K have been estimated to be 0.24, 2.8 and 1.8, respectively. The limiting activity coefficients of $AgS_{0.5}$ in iron-copper mattes have been calculated at 1473 K based on the experimental

data of the present investigation, assuming the matte phase to be a $CuS_{0.5-x}$ -FeS-$AgS_{0.5}$ pseudo-ternary solution. The calculated values have been represented by the expression, $\gamma^{\circ}_{AgS_{0.5}} = 0.80 + 6600\,(N_{Fe})^6$.

7. Thermodynamic Consideration on the Behavior of Ag, Se and Te in Copper Smelting Process

In Chapter 7, the experimental data obtained in the present investigation have been evaluated thermodynamically to predict the behavior of the minor elements in the copper smelting process. As to the vaporization behavior, the analysis showed that the total pressure of silver, as the sum of the elemental, sulfidic and oxidic contributions is the highest compared to those of Se and Te. Although the monatomic Se and Te are the prevailing gas species of the elements at the smelting conditions, monoxide SeO and TeO become more volatile in the converting process with the oxygen potential becoming intense toward blister copper. The limiting Raoultian activity coefficient of silver oxide as $AgO_{0.5}$ in the calcium ferrite slag coexisted with liquid copper was calculated to be 3.3 at 1523 K. It was shown that the limiting activity coefficient is independent of the oxygen potential. The effect of dissolved oxygen on the limiting activity coefficients of the minor elements has been evaluated. The limiting activity coefficients of the minor elements in white metal were correlated with the solubility of oxygen in the blister copper. It was shown that oxygen lowers the activity coefficients of Ag and particularly Se and Te, but it does not change the order of the activity coefficient values at the practical oxygen solubilities.

8. Conclusions

In Chapter 8, the main conclusions by the result of the present thesis are given. The distribution ratio of silver, {mass%Ag}/[mass%Ag], decreases from 0.39 in the iron-free systems to 0.28 at iron-saturation. The addition of iron promotes the distribution ratio of Se from 13.5 in the Cu-S system to about 19 near iron saturation, while that of Te reduces from 9 in the Cu-S system to about 8 near iron saturation. The limiting activity coefficients of Ag, Se and Te in the iron-free matte at 1473 K were found to be 9.9, 5.6×10^{-4} and 9.3×10^{-3}, respectively. The limiting activity coefficients of the minor elements have been correlated to the iron content of matte. The addition of iron beyond about 10 at% increases the limiting activity coefficients of Ag and Te in the matte phase, while it does not affect that of Se. The calculated total pressures of Ag, Se and Te over the equilibrium copper-matte system indicate that remarkable losses of the minor elements by vaporization are not practically expected in the converting process. The partial pressure of the sulfidic and oxidic forms of the minor elements are negligible compared with those of the elemental form in the moderate oxidizing conditions. However, the monoxides SeO and TeO increasingly become more volatile toward the blister making stage.

審査結果の要旨

有価元素の回収および有害元素の除去との関連で銅のマット溶錬において重視されている微量成分の制御の基本として，Cu-Fe-S系および Cu-S系マット中の微量成分の熱力学データが重要であるが，熱力学的性質に関する研究事例は少ない。本論文は，銅マットの酸化溶錬および還元溶錬において出現する金属相とマット相との２相共存組成域におけるAg, Se, Teの活量を多重クヌーセンセル質量分析法により求め，これらの成分の活量係数，相互作用係数などを導出したもので，全編８章からなる。

第１章は緒論であり，本研究の意義と目的について述べている。

第２章では，活量測定に用いた多重クヌーセンセル質量分析法の原理と装置の構成について述べ，測定試料と参照試料が呈する揮発ガスのイオン強度比を同一条件において求める本方法が原理的に優れたものであることを示している。

第３章では，Cu-Ag, Cu-Se各２元系合金の活量を1473Kで測定し，一方，Cu-Te２元系合金の活量に関する文献データを評価している。また，これらの２元系合金の活量データが，銅ーマット系に対する Ag, Se, Te の活量測定用の参照データとして十分な精度を有することを示している。

第４章では，銅ーマット系の２相共存関係に及ぼすAg, Se, Teの添加の影響を1473K で調べ，多重クヌーセンセル質量分析法による活量測定の基本データとして必要とされる２液相共存組成を決定している。

第５章では，Cu-Cu_2S２相共存組成域における Ag, Se, Teの活量を測定し，金属銅およびCu_2S中の無限希薄における活量係数を導出するとともに，溶銅中の活量係数に対する硫黄の第一次相互作用係数を求めている。

第６章では，銅ー鉄合金相とCu-Fe-S系マット相とが共存する組成域における活量を1473K で測定し，マット中の Ag, Se, Te の無限希薄における活量係数をマットの鉄濃度の関数として導出している。また，銅ー鉄合金中の Ag, Se, Te の活量係数に対する鉄の第一次相互作用係数を求めている。

第７章では，上記研究により得られた熱力学データを用いて，銅マットの酸化溶錬および還元溶錬におけるガス中の Ag, Se, Te の形態と分圧を評価，算出し，またマットと平衡するスラグ中の活量係数を導出することにより，揮発および分配によるこれらの成分の除去ないしは回収の可能性について検討している。

第８章は，本研究の全体から得られた結果の総括である。

以上要するに本論文は，銅ーマット系における微量成分 Ag, Se, Te の熱力学データを多重クヌーセンセル質量分析法を用いて系統的に測定，集積し，銅の酸化溶錬および還元溶錬工程における不純物制御の指針について考究したもので，金属工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。